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Bromine



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Bromine

By Phyllis A. Lyday¹

Of the 847 million pounds of bromine produced worldwide in 1987, the United States produced 40%, followed by Israel, 27%; the U.S.S.R., 17%; the United Kingdom, 6%; and other countries, 10%. The

U.S. portion of world production has decreased steadily since 1973, when the United States produced 71% of the world supply. The decrease in world share has been a result of environmental constraints

Table 1.—Salient bromine and bromine compound statistics

(Thousand pounds and thousand dollars)

	1983	1984	1985	1986	1987
United States:					
Bromine sold or used: ¹					
Quantity	370,000	385,000	320,000	310,000	^a 335,000
Value	\$91,000	\$95,000	\$80,000	\$93,000	^a \$107,000
Exports:					
Elemental bromine:					
Quantity	² 4,500	³ 68,200	² 6,252	² 17,900	² 7,380
Value	² \$1,000	² \$15,200	² \$1,400	² \$8,170	² \$3,526
Bromine compounds: ⁴					
Gross weight	61,300	53,200	61,000	28,000	48,300
Contained bromine	52,000	45,100	51,900	23,000	41,100
Value	\$21,600	\$16,200	\$23,400	\$23,900	\$18,000
Imports:²					
Elemental bromine:					
Quantity	(⁵)	9	11	342	547
Value	\$5	\$17	\$9	\$87	\$166
Compounds:					
Ammonium bromide:					
Gross weight	1,634	1,450	2,786	5,721	4,946
Contained bromine	1,333	1,183	2,729	4,667	3,778
Value	\$962	\$854	\$1,593	\$2,994	\$2,257
Calcium bromide:					
Gross weight	1,722	1,598	5,093	6,218	8,075
Contained bromine	1,377	1,278	4,072	4,972	6,456
Value	\$900	\$203	\$917	\$741	\$833
Potassium bromate:					
Gross weight	679	661	1,069	641	3,063
Contained bromine	325	350	512	340	1,466
Value	\$572	\$610	\$899	\$669	\$849
Potassium bromide:					
Gross weight	436	367	968	697	1,910
Contained bromine	293	246	650	468	1,282
Value	\$303	\$268	\$685	\$486	\$1,122
Sodium bromide:					
Gross weight	2,534	1,916	2,901	467	1,448
Contained bromine	1,927	1,488	2,253	364	1,124
Value	\$971	\$851	\$1,108	\$217	\$507
Other:					
Gross weight	12,070	15,150	10,987	10,112	18,286
Contained bromine	10,241	11,535	6,863	8,004	11,220
Value	\$8,105	\$8,210	\$5,863	\$4,627	\$13,607
World: Production	801,863	875,150	839,982	^b 824,380	^c 846,530

^aEstimated. ^bPreliminary.

¹Elemental bromine sold as such to nonproducers, including exports, or used in the preparation of bromine compounds by primary U.S. producers.

²Bureau of the Census.

³The Journal Commerce Port Import/Export Reporting Service.

⁴Bureau of the Census. Includes methyl bromide and ethylene dibromide.

⁵Less than 1/2 unit.

and the emergence of Israel as a major producer. The quantity of bromine sold or used in the United States was about 335 million pounds valued at \$107 million. Exports of bromine compounds amounted to 41.1 million pounds. The price of elemental bromine in bulk was 35 cents per pound. Primary uses of bromine compounds were as a scavenger for lead in gasoline, oil and gas well fluids, and flame retardants.

Domestic Data Coverage.—Domestic production data for bromine are developed by the Bureau of Mines from a voluntary survey of U.S. operations. Of the eight operations to which a survey request was sent, all responded, representing 100% of total elemental bromine sold or used.

Legislation and Government Programs.—The Environmental Protection Agency (EPA) undertook a special review of the ethylene dibromide fungicides: Mancozeb, Maneb, Metiram, Nabam and Zineb.²

An amendment to the New York State Fire Prevention and Building Code went into effect at yearend. New York was the first State to require all plastic products marketed in the State, regardless of where manufactured, to be tested for toxicity before being sold. Major products being tested were electrical conduit wire, pipe, and duct insulation, which can use brominated flame retardants to meet building codes.³

Great Lakes Chemical Corp. and the Arkansas State Pollution Control and Ecology Department agreed to a number of environmental improvements at the El Dorado plant over a 3-1/2-year period. The agreement was a result of an October 1985 notice of violation. Improvements included repairing or closing some waste collection ponds, treating waste water in a new facility, cleaning up ground water contamination, and increasing ground water monitoring. Great Lakes constructed a new facility for treating waste water. Additional recovery wells will pump contaminated water from the ground to be treated in the new waste water facility. Additional monitoring wells will also be installed. If any parts of the plan are not completed on time, Great Lakes will pay penalties from \$500 to \$2,500 per day.⁴

EPA approved the registration of bromine chloride, EPA Reg. No. 5785-68, and bromine chloride technical, EPA Reg. No. 337-20. Both products are classified for general use as a algicide, bactericide, disinfectant, and slimicide in waste water, commercial, and industrial recirculation cooling water systems.⁵

A final test rule was issued by EPA that required manufacturers and processors of tetrabromobisphenol-A, a major brominated flame retardant, to perform testing for chemical and environmental effects. The testing requirements included biodegradation studies in sediment/water and soil, an acute toxicity study in a freshwater alga, acute and early life state toxicity studies in fish, a partial life-cycle toxicity study in a benthic invertebrate, a chronic toxicity study in an aquatic invertebrate, and bio-concentration studies in fish and invertebrate.⁶

The incineration of 328,000 gallons of ethylene dibromide (EDB) was being considered by EPA as a method to dispose of the chemical. A test was planned in December of the incineration process. EDB was banned as a fumigant in September 1985, and manufacturers and distributors quickly surrendered all stocks of the chemical for disposal.⁷

Ten brominated chemicals were controlled for national security reasons under Export Control Commodity No. 5799D. The U.S. Department of Commerce undertook a review of the rationale for the controls and decided to terminate the control of these chemicals on the grounds that the availability of these chemicals would no longer make a significant contribution to the military potential. The decision was made in consultation with the U.S. Departments of Defense, Energy, and State. The chemicals remain subject to export controls to Country Groups S and Z for foreign policy reasons.⁸

In California, 1,2 dibromo-3-chloropropane was listed as 1 of 29 toxic substances under proposition 65, the Safe Drinking Water & Toxic Enforcement Act (Superfund) of 1986. Under the provisions of the law, businesses are prohibited from discharging listed chemicals into drinking water unless the discharged amounts can be shown to be safe. Businesses are also prohibited from exposing individuals to listed chemicals at unsafe levels without first warning them of the risk.⁹

The U.S. Department of Health and Human Services and the EPA published a priority list for toxicological profiles of 100 hazardous substances found at Superfund sites. The list included four brominated compounds in priority groups 2, 3, and 4. The list was prepared from 717 hazardous substances currently identified at Superfund sites.¹⁰

The Arkansas State Plant Board, the

Mississippi Department of Agriculture and Commerce, and the Louisiana Agriculture Department granted a section 18 exemption for bromoxynil for control of hemp sesbania, morning glory, and cocklebur in rice. The exemption expired August 1, 1987.¹¹

The Office of the Governor, Territory of Guam, granted a section 18 quarantine exemption for the use of methyl bromide to control western flower thrips and cabbage aphids on several vegetables. The exemption expires January 12, 1991.¹²

DOMESTIC PRODUCTION

Three companies representing the U.S. Bromine Alliance accounted for about 95% of U.S. elemental bromine capacity. Plant capacity did not reflect production capacity, which was dependent upon brine supplies, concentration of the bromine in the brine, and individual plant extraction processes. Arkansas brines contained about 6,000 parts per million and Michigan brines about 2,600 parts per million of bromine.

Ethyl Corp. concluded an agreement with The Dow Chemical Co. to purchase Dow's facility in Magnolia, AR, and other bromine assets. Included was the brine field leases in the Magnolia area, distribution equipment, facilities, and inventories worldwide, as well as certain patents pertaining to Dow's bromine chemical technology. Under a consent decree reached with the U.S. Department of Justice, Dow and Ethyl agreed to exclude Dow's brominated clear brine fluids business from the transaction. As part of the consent decree, Dow will attempt to sell its brominated clear brine fluids business to a qualified purchaser. Dow will continue to operate a plastic foam plant on the Magnolia site until the plant can be relocated.

Ethyl assumed sales activities for Dow's elemental bromine, flame retardants, organic bromides, and sodium hydrosulfide. Ethyl will integrate operations for the former Dow bromine chemical facility with its existing operations in Magnolia and will construct new facilities at both sites to

manufacture products Dow produced in Midland, MI. New facilities are also under construction at Magnolia to produce flame retardants formerly produced in Sayreville, NJ.

Morton Thiokol Inc. produced small quantities for captive use in inorganic bromides. Rhône-Poulenc S.A. through its subsidiary, the France-based inorganic bromide producer Potasse et Produits Chimiques (PPC), bought Morton's current inventory and technology for inorganic bromides, which are primarily used in photography. Rhône-Poulenc Inc. (USA) will function as PPC's U.S. sales agent.¹³

Great Lakes, which operated three bromine plants in Union County, announced a 50% expansion of a plant in Adrian, MI, that produces bromochlorodimethylhydantoin, a bromine-containing biocide used in a variety of applications, including swimming pools, spas, cooling towers, and waste water treatment.¹⁴

Great Lakes purchased QO Chemical Inc., a wholly owned subsidiary of Pentech Corp. QO produced furfural from agricultural waste and then manufactured furyl alcohol and other specialty products used in building materials, chemical intermediates, flame retardants, foundry resins, oil refining, plastics, and urethane systems. The new company will use many of the brominated flame retardants that Great Lakes produce.

Table 2.—Bromine-producing plants in the United States in 1987

State and company	County	Plant	Production source	Elemental bromine plant capacity ¹ (million pounds)
Arkansas:				
Arkansas Chemicals Inc.	Union	El Dorado	Well brines	50
The Dow Chemical Co.	Columbia	Magnolia	do	110
Ethyl Corp.	do	do	do	160
Great Lakes Chemical Corp.	Union	El Dorado	do	105
Do	do	Marysville	do	80
Do	do	El Dorado	do	50
Michigan:				
The Dow Chemical Co.	Mason	Ludington	do	20
Morton Thiokol Inc.	Manistee	Manistee	do	5
Total				580

¹Chemical Marketing Reporter, Chemical Profile, V. 228, No. 4, July 22, 1985, pp. 53-54.

CONSUMPTION AND USES

The U.S. International Trade Commission publication, "Synthetic Organic Chemicals, 1986" reported that the Dyes & Pigments Div. of Mobay Chemical Corp. produced Pigment Red No. 168, dibromoanthranthrone orange. Red No. 168 was used in automotive metallic applications because of its transparency.

Demand for EDB, primarily as a gasoline additive, reached a low of about 10% of total consumption. Fire retardants were estimated to be about 30% of consumption, primarily as tetrabromobisphenol-A and decabromodiphenyl oxide. Agriculture uses were about 10% of consumption, principally as methyl bromide used as a soil fumigant. Bromine is used in water treatment as a slime and biocidal control product. Sodium bromide was estimated at about 5% of consumption. About 30% of bromine consumption was as calcium bromide in work-over and completion fluids. Other uses were estimated at approximately 15% of consumption.¹³

According to data from the Bureau of the Census, 1 billion pounds of bisphenol-A was produced in 1987, up 21% from production in 1986. The demand was strong in the polycarbonate resin sector, which amounts to approximately one-half of the market. Epoxy resins, which account for about one-third of the market, were also strong.¹⁴ Tetrabromobisphenol-A is a major flame retardant produced from bisphenol-A, used

in epoxy, polyester, and other polymers where low color and high clarity are mandatory.¹⁵ A study of flame retardants consumption by polymers estimated 36 million pounds of bromine additives was used in 1986. The majority was in polyacrylonitrile-butadiene-styrene and polystyrene products.¹⁶

Bromine was used in biocides in recirculatory cooling systems. Formulated alone or with other active ingredients, bromine compounds are regarded by the water treatment industry as cost-effective biocides. Some compounds have both bacteriostatic and fungistatic properties at low concentrations.¹⁷

Bromine added as a bromide salt with chlorine or hypochlorine leaches gold as well as platinum in acid, neutral, or alkaline water. A product marketed under the name "Bio-D Leachant", being distributed in North America, has been reported as a better reagent than bromocide, a disinfectant, because it is readily recycled for reuse. About 20 small operators were reported to be using bromine. Three larger companies were testing bromine on 5,000-short-ton heap-leaching operations. The advantages of bromine are rapid extraction, nontoxicity, and adaptability to a wide range of conditions. Disadvantages are high reagent consumption and interferences in standard assay techniques.²⁰

PRICES

Bromine was sold under contracts negotiated between buyer and seller. Price quotations do not necessarily represent prices at which transactions actually occurred, nor

do they represent bid and asked prices. They were quoted here to serve only as a guide to year-end price levels.

Table 3.—Yearend 1987 prices for elemental bromine and selected compounds

Product	Value per pound (cents)
Ammonium bromide, National Formulary (N.F.), granular, drums, carlots, truckloads, freight equalized, f.o.b. works	131
Bromine, purified:	
Purified, truckloads, delivered	77
Drums, truckloads, works ¹	87
Bulk tank car, tank trucks (45,000-pound minimum), delivered east of the Rocky Mountains ¹	35
Bromochloromethane, drums, carlots, f.o.b. Midland, MI	112
Calcium bromide, bulk, 14.2 pounds per gallon at 60° F, f.o.b. works ²	20-
Ethyl bromide, technical, 98%, drums, carlots, freight allowed, East	21
Ethylene dibromide, drums, carlots, freight equalized	5-
Hydrobromic acid, 48%, drums, carlots, truckloads, f.o.b.	46
Hydrogen bromide, anhydrous, cylinders, extra 30,000 pounds, f.o.b. works	38.5
Methyl bromide, distilled, tanks, 140,000-pound minimum, freight allowed	700
Potassium bromate, granular, powdered, 200-pound drums, carlots, f.o.b. works	56.75
Potassium bromide, N.F., granular, drums, carlots, f.o.b. works	106
Sodium bromide, 99% granular, 400-pound drums, freight, f.o.b. works	112
	104

¹Delivered prices for drums and bulk shipped west of the Rocky Mountains, 1 cent per pound higher. Bulk truck prices 1 to 2.5 cents per pound higher for 30,000-pound minimum and 4 to 5.5 cents per pound higher for 15,000-pound minimum.

²Reported to the Bureau of Mines by primary producers.

Source: Chemical Marketing Reporter. Current Prices of Chemicals and Related Materials. V. 232, No. 26, Dec. 28, 1987, pp. 28-36.

FOREIGN TRADE

AmeriBrom Inc., a member of the Israeli Dead Sea Bromine Co. Ltd., a part of Israel Chemicals Ltd., began to ship larger quantities of elemental bromine to the United States because of an increase in demand. Previous market commitments to Europe and Japan limited the amount of bromine

that could be shipped to the United States. Imports from Israel and from Broomchemie BV in the Netherlands had been primarily in the form of derivatives in previous years. Morre-Tec Industries Inc. of Union, NJ, was appointed distributor of calcium bromide for AmeriBrom.

WORLD REVIEW

Canada.—In Alberta, formation waters with bromide contents greater than 1,000 milligrams per liter are confined to small areas in the Upper Devonian Winterburn and Woodbend Groups of central Alberta; the Upper Devonian Beaverhill Lake Formation of southern Alberta; the Middle Devonian Elk Point Group of north-central Alberta; and the Granite Wash, northern Alberta. Formation water from the Beaverhill Lake Formation of southern Alberta contained nearly 2,790 milligrams per liter of bromide, which corresponds to the concentration of brines at Midland, MI, but less than the 5,000 parts per million for Arkansas brines and the 12,000 parts per million for bitterns from potash production from the Dead Sea.²¹

China.—An underground deposit near Laizhou Bay, Shandon, reported reserves at 600 million cubic meters of brine.²²

Europe.—An expert panel was studying ways to curb salt spills into the Rhine from French sources. France (30%), the Federal Republic of Germany (30%), the Netherlands (34%), and Switzerland (6%) will split

the budget of the panel. One plan suggested doubling existing storage facilities to cope with the 16 million tons of salt coming from the Mines de Potasse d'Alsace S.A., at Amelie. Bromine is produced as a byproduct of potash production in France and the Federal Republic of Germany.²³

France.—Mines de Potasse d'Alsace was in the process of building an additional bromine column to bring the total columns to 10. The glass columns are about 4 feet wide and produce a combined total of 13 tons per day of elemental bromine.

Germany, Federal Republic of.—Kali und Salz AG reported that the only potash mine in production was the Salzdetfurth Mine with an annual bromine capacity of 5.5 million pounds. The mine is north of Kassel between the Leine and Oker Rivers.

Because of concern by the Green Party, the Verband Der Chemische Industrie announced in 1985 a voluntary, precautionary action to reduce and possibly eliminate the use of brominated flame retardants in plastics. A group of world producers formed the Brominated Flame Retardant Industry

Panel (BFRIP) to investigate reports that researchers in the Federal Republic of Germany, Switzerland, and the United States had reported finding significant quantities of brominated dioxins and furans in brominated diphenyl oxide flame retardants. To address the issues, BFRIP developed a program to test the animal toxicity of the solid decomposition products of polymers containing brominated flame retardants under combustion conditions.²⁴

Other studies released during 1987 complement the work being funded by the BFRIP. Dow, a member of the BFRIP, released a study that indicates humans exposed to dioxins generally experienced death rates at or below those of a corresponding United States population.²⁵ Scientists report no evidence of an increase in birth defects following a 1976 accident in Seveso, Italy, that exposed the surrounding population to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Several small animals were found dead at the time of the TCDD expo-

sure but, other than choracne, a severe form of acne, no other effects were observed in exposed humans. The study concluded that the rates of both major and minor malformations are the same in TCDD-exposed areas as in nonexposed areas.²⁶

Israel.—Dead Sea Bromine Co. Ltd., Sdom, announced a proposed expansion of 265 million pounds costing \$150 million.²⁷ Israel Chemicals, the parent of Dead Sea Bromine, was developing a new calcium bromide process to extract calcium bromide directly from brines. In addition, a process for organic solvent extraction of calcium bromide from potash bitterns was being developed to delete an intermediate energy consuming step. Conventional methods react hydrogen bromide with calcium hydroxide. The Israelis have operated a pilot plant of 2 to 4 million pounds per year since 1984. It was reported that a demonstration facility was being built to test the new calcium bromide process.²⁸

Table 4.—World bromine plant capacities and sources

Country and company	Location	Capacity (million pounds)	Source
China:			
Laizhou Bromine Works	Shandong	1	Underground brines.
France:			
Atochem	Port-de-Bouc	30	Seawater.
Mines de Potasse d'Alsace S.A.	Mulhouse	19	Bitterns of mined potash production.
German Democratic Republic:			
Government	Bleicherode	NA	Do.
	Sondershausen	NA	Do.
Germany, Federal Republic of:			
Kali und Salz AG: Salzdettfurth Mine	Bad Salzdettfurth	5.5	Do.
India:			
Hindustan Salts Ltd.	Jaipur	1.6	Seawater bitterns from salt production.
Mettur Chemicals	Mettur Dam		
Tata Chemicals	Mithapur		
Israel:			
Dead Sea Bromine Co. Ltd.	Sdom	220	Bitterns of potash production from surface brines.
Italy:			
Società Azionaria Industriale Bromo Italiana	Margherita di Savoia	2	Seawater bitterns from salt production.
Japan:			
Asahi Glass Co. Ltd.	Kitakyushu	9	Seawater bitterns.
Toyo Soda Manufacturing Co. Ltd.	Tokuyama	44	Do.
Spain:			
Derivados del Etilo S.A.	Villaricos	2	Seawater.
U.S.S.R.:			
Government	NA	150	Well brines.
United Kingdom:			
Associated Octel Co. Ltd.	Amlwch	66	Do.

NA Not available.

Table 5.—Bromine: World production, by country¹

(Thousand pounds)

Country ²	1983	1984	1985	1986 ³	1987 ⁴
France ⁵	35,000	38,600	44,000	42,000	41,000
Germany, Federal Republic of	6,914	7,288	6,784	*5,500	5,500
India ⁶	770	770	770	770	770
Israel ⁶	154,000	198,400	220,000	231,500	231,500
Italy ⁶	1,100	1,100	1,320	990	1,100
Japan ⁶	26,500	26,500	26,500	*33,000	33,000
Spain ⁶	700	660	800	620	660
U.S.S.R. ⁶	150,000	154,000	154,000	143,000	143,000
United Kingdom	56,879	62,832	65,808	*57,000	55,000
United States ³	370,000	385,000	320,000	310,000	*335,000
Total	801,863	875,150	839,982	824,380	846,530

⁵Estimated. ⁶Preliminary. ⁷Revised.¹Table includes data available through May 6, 1988.²In addition to the countries listed, several other nations produce bromine, but output data are not reported, and available general information is inadequate for formulation of reliable estimates of output levels.³Sold or used by producers.⁴Reported figure.

TECHNOLOGY

Greater solubilities for some metals occur in the metal bromide-hydrogen, bromide-water system. Stricter control of effluents and declining ore grades have caused an increase in interest in hydrometallurgical processing. Bromide reagents are more costly than chloride reagents, but recycling the reagents would minimize the difference and increase demand for bromine compounds for use in metallurgical processing. Solubility studies of various metal bromides reported crystallization was almost total at hydrogen bromide saturation for aluminum bromide, potassium bromide, and sodium bromide.²⁹

The bromine number is defined as the number of grams of bromine that reacts with 100 grams of a substance under certain conditions. The ASTM D 1159-77 method for determining the bromine number of petroleum products with boiling points to 327° C was modified to make it suitable for products up to 550° C.³⁰

A radioactive bromine had been used to treat ovarian and estrogen-dependent cancers. The treatment employs an estrogen-like drug to which the radioactive bromine is attached. The drug binds to a cell that locates bromine close to the genetic material. As the bromine decays, it destroys the cell's structure. The drug will undergo animal tests before human trials.³¹

Interest has intensified in annual shrinkage of the stratospheric ozone layer over the Antarctic. Bromine and bromine monoxide are two of the halogen species being studied by scientists around the world for their part

in the reactions that destroy ozone. If bromine is determined to be a major factor, the demand for bromine could be affected by world bans, such as those placed on chlorofluorocarbons (CFC).³² A draft treaty was reached by 28 countries during negotiations sponsored by the United Nations Environmental Program. Halons 1211 and 1301, both containing bromine, are not covered by the proposal.³³ The U.S. Congress was considering legislation to curb further use of CFC, including Halons 1211 and 1301, thus decreasing demand for bromine.

A method for classification and identification of air pollutants, including brominated hydrocarbons, was developed. The compounds are identified by comparing their data with the three nearest neighbors in the set. The classification accuracy was 85%.³⁴ This method could increase the accuracy of identification of brominated compounds for making policy decisions on polluting compounds.

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